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60/418,519 15 October 2002 (15.10.2002) US
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- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: ATOMIC LAYER DEPOSITION OF NOBLE METALS

(57) Abstract: The present invention relates to ALD processes for deposition of a metal selected from Pd, Rh, Ru, Pt and Ir wherein a layer including the metal is formed on a surface composed of a material selected from W, Ta, Cu, Ni, Co, Fe, Mn, Cr, V Nb, tungsten nitride, tantalum nitride, titanium nitride, dielectrics and activated dielectrics at a temperature ranging from >60°C to <260°C. The layer is formed by sequentially pulsing into a chamber containing said surface a precursor for the metal and a reducing gas selected from hydrogen, glyoxylic acid, oxalic acid, formaldehyde, 2-propanol, imidazole and plasma-activated hydrogen.

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INTERNATIONAL SEARCH REPORT

International Application No

US 03/32644

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C23C16/14 C23C16/448 C23C16/455

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2002/081381 A1 (LU TOH-MING ET AL) 27 June 2002 (2002-06-27) *pages 1 and 2, [0007] to [0009] and [0012] to [0014]; [0028]* -----	1,2, 13-17
X	WO 01/88972 A (ASM MICROCHEMISTRY OY ;SOININEN PEKKA JUHA (FI); ELSERS KAI ERIK (F) 22 November 2001 (2001-11-22) *page 7, line 3; page 15, lines 13-17; page 16, line 18; page 17, lines 11-18; claims 17-19* -----	1,2
X	WO 02/45167 A (ASM MICROCHEMISTRY OY ;HUJANEN JUHA (FI); RAAIJMAKERS IVO (NL); AS) 6 June 2002 (2002-06-06) *page 5, line 22 to page 6, line 18* ----- -/--	1,2

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

6 May 2004

Date of mailing of the international search report

23.07.04

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INTERNATIONAL SEARCH REPORT

International Application No

PO/US 03/32644

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with Indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>US 2002/031618 A1 (SHERMAN ARTHUR)</p> <p>14 March 2002 (2002-03-14)</p> <p>the whole document</p> <p>-----</p>	<p>1,2,</p> <p>13-17</p>

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 03/32644

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1, 2, 13 - 17

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1,2,13-17

Method claims 1, 2 and 13 to 17 are directed towards an ALD process for depositing a metal layer of Pd, Rh, Ru, Pt or Ir on a surface comprising a material selected from W, Ta, Cu, Ni, Co, Fe, Mn, Cr, V, Nb, tungsten nitride, tantalum nitride, titanium nitride and dielectrics at a temperature range of 60°C to 260°C.

2. claims: 3-11

Method claims 3 to 11 are directed towards an ALD process for depositing a metal layer of Pd, Rh, Ru, Pt or Ir on a surface comprising a material selected from noble metals, W, Ta, Cu, Ni, Co, Fe, Mn, Cr, V, Nb, tungsten nitride, tantalum nitride and titanium nitride by pulsing a precursor for the metal at a temperature range of 60°C to 260°C and pulsing a reducing gas.

3. claim: 12

Method claim 12 is directed towards an ALD process for depositing a metal layer of Pd, Rh, Ru, Pt or Ir on a substrate by pulsing a precursor for the metal at a temperature range of 60°C to 260°C and pulsing plasma-activated hydrogen gas.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US 03/32644

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 2002081381	A1	27-06-2002	NONE	
WO 0188972	A	22-11-2001	AU 6037401 A	26-11-2001
			EP 1282911 A1	12-02-2003
			WO 0188972 A1	22-11-2001
			JP 2003533880 T	11-11-2003
			TW 508658 B	01-11-2002
			US 2004038529 A1	26-02-2004
			US 2003096468 A1	22-05-2003
			US 2004005753 A1	08-01-2004
			US 2002004293 A1	10-01-2002
			US 2002098685 A1	25-07-2002
			US 2002092584 A1	18-07-2002
WO 0245167	A	06-06-2002	AU 2576102 A	11-06-2002
			EP 1340269 A2	03-09-2003
			TW 527700 B	11-04-2003
			WO 0245167 A2	06-06-2002
			US 2002076837 A1	20-06-2002
US 2002031618	A1	14-03-2002	US 6342277 B1	29-01-2002
			US 5916365 A	29-06-1999
			EP 1183406 A1	06-03-2002
			JP 2002541332 T	03-12-2002
			WO 0061833 A1	19-10-2000
			US 2004076751 A1	22-04-2004
			US 2004083949 A1	06-05-2004
			US 2001028924 A1	11-10-2001